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(54) Manufacturing method of resin granules.

(57) The present invention provides the method which enables to manufacture substantially spherical resin granules with narrow grain size distribution by a simple operation. The present invention provides the manufacturing method of resin granules with grain diameter of 1 - 100 µm and narrow grain size distribution by controlling cloud point of polyvinyl alcohol and other water-soluble polymer.

EP 0 542 051 A1

**Field of The Invention**

The present invention relates to a manufacturing method of resin granules with narrow distribution of grain diameter, in particular a manufacturing method of granules useful for toner for electrostatic recording and the carrier of diagnostic agent.

**Background of The Invention**

Various examinations have been made in regard to the manufacturing method of micron-size resin granules with narrow distribution of grain size and many patents have been filed.

One of such methods is the so-called suspension-polymerization method wherein liquid drops of vinyl monomer are formed in water in the presence of an appropriate dispersion stabilizer and polymer granules are synthesized using appropriate oil-soluble polymerization initiator.

However when polymerization is conducted under the ordinary agitating conditions, the polymer sticks to the wall of the reaction vessel, agitating fan etc and when polymer granules are produced, distribution of grain diameter is mostly governed by the probability factor of division and joining of liquid drops during polymerization and as the result only those having extremely wide grain size distribution are obtained. As the countermeasure therefor, they proposed the method wherein polymerization conditions are so modified that, for example, the monomer once goes through bulk polymerization or a part of the polymer is dissolved in the monomer and after thus providing some viscosity, suspension polymerization is conducted or the method wherein polymerization is conducted by using various suspension stabilizer having strong surface activity or inorganic powder hard to dissolve in water or co-using them but the improvement of grain size distribution realized has been only slight.

On the other hand, according to the seed polymerization swelling method described in Japanese Kokai Publication 58-106554, it is possible to form the vinyl polymer granules of extremely narrow grain size distribution and it is also possible to bridge and gelate the monomer using polyfunctional monomer such as divinyl benzene.

However according to this method, growth of grain occurs in multi-stages and therefore the steps are extremely long and thus its industrialization potential is poor and besides it is difficult to uniformly charge foreign matters such as pigment in the granules.

In order to improve such drawbacks, for example, Japanese Kokai Publication 3-200976 proposes the method of forming colored polymer granules by dispersion polymerization in non-aqueous (or solvent/water mixture) solvent. However since the method uses solvent, problems occur as to waste liquid treatment and safety.

**Summary of The Invention**

The present invention solves the aforesaid conventional problems and its objective is to provide the method which enables to manufacture by simple and convenient process the substantially spherical resin granules with narrow grain size distribution.

The present invention thus provides manufacturing method of resin granules with grain diameter 1 ~ 100 µm and narrow grain size distribution comprising mixing the following three components:

(a) either polyvinyl alcohol with cloud point at 30 ~ 90°C obtained by addition of electrolytic salt to the aqueous solution of polyvinyl alcohol with saponification degree of more than 85 % or polyvinyl alcohol with saponification degree of 60 ~ 85 %, or the both

(b) an aqueous solution containing at least one kind of water-soluble polymer selected from the group consisting of methyl cellulose, hydroxypropyl cellulose, polyethylene glycol alkyl ether and block copolymer of polyethylene glycol-polypropylene glycol, and

(c) a granule forming component containing a polymerizing monomer,

at the temperatures below the cloud point of polyvinyl alcohol and water-soluble polymer, thus obtaining fine primary granules of less than 10 µm, heating such primary granules to the temperature above said cloud point to obtain by agglomeration and unification of such granules, substantially spherical granules with grain diameter having increased to about 2 ~ 20 times, and then polymerizing them during heating or after formation of granules.

The present invention also provides manufacturing method of resin granules with grain diameter 1 to 100 µm and narrow grain size distribution, comprising mixing the following two components:

(a) either polyvinyl alcohol with cloud point at 30 to 90°C obtained by addition of electrolytic salt to the aqueous solution of polyvinyl alcohol with saponification degree of more than 85 %, or polyvinyl alcohol

with saponification degree of 60 to 85%, or the both, and  
 (c) a granule forming component containing a polymerizing monomer,  
 at the temperatures below the cloud point polyvinyl alcohol and water-soluble polymer mentioned herein-  
 after, thus obtaining fine primary granules of less than 10 µm, admixing with  
 5 (b) an aqueous solution containing at least one kind of water soluble polymer selected from the group con-  
 sisting of methyl cellulose, hydroxypropyl cellulose, polyethylene glycol alkyl ether and block copolymer  
 of polyethylene glycol-polypropylene glycol,  
 at the temperatures below the cloud point, heating such primary granules to the temperature above said cloud  
 point to obtain, by agglomeration and unification of such granules, substantially spherical granules with grain  
 10 diameter having increased to about 2 to 20 times, and then polymerizing them during heating or after formation  
 of granules.

#### Detailed Description of The Invention

15 Polyvinyl alcohol having cloud point in the range of 30 ~ 90°C used in the present invention is the one  
 having been given such cloud point by addition of electrolytic salt to polyvinyl alcohol with saponification degree  
 of more than 85 % or polyvinyl alcohol with saponification degree of 60 to 85 %.

Water souble polymer having cloud point in the range of 30 ~ 90°C used in the present invention is chosen  
 out of the group comprising cellulose derivatives such as methyl cellulose hydroxypropyl cellulose, polyethy-  
 20 lene glycol alkyl ether and block copolymer of polyethylene glycol-polypropylene glycol.

The polymerizable monomer usable for the grain forming components of the present invention may be a  
 monomer with ethylenic unsaturated double bond or a compound which can make interfacial polymerization  
 reaction. The monomer with ethylenic unsaturated double bond may be styrene-based monomer or acrylic acid  
 ester-based monomer. Styrene-based monomer may be styrene, vinyl toluene, ethyl styrene, p-chlorostyren ,  
 25 etc. Acrylic ester monomer may be ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate,  
 methyl acrylate, methyl methacrylate, 2-ethylhexylacrylate, 2-ethylhexyl methacryate etc. These monomers  
 may be used independently or in a mixture and when necessary, they may be co-used with N,N'-dimethyl-  
 aminoethyl methacrylate N,N'-diethylaminoethyl methacrylate or cathionic monomer such as vinyl pyridine r  
 30 amionic monomer such as unsaturated fatty acid and unsaturated fatty acid anhydride such as acrylic acid,  
 methacrylic acid, maleic acid, fumaric acid and maleic acid anhydride. Further the polyfunctional monom r  
 such as divinyl benzene, ethylene glycol dimethacrylate, trimethylol propane triacrylate, glycidyl metacrylate,  
 glycidyl acrylate, etc.

The compounds which can make interfacial polymerization reaction are organic-soluble compounds with  
 more than two groups available for chemical reaction per molecule and can form polymer layer at the out r  
 shell of the granule by reacting with water-soluble monomer having more than two functional groups, to be  
 35 more specific, diisocyanate compounds such as diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohex-  
 ylmethane diisocyanate, m-tetramethylxylene diisocyanate (m-TMXDI), trimethylhexamethylene diisocyanate  
 (TMDI), hexane diisocyanate, diisocyanate prepolymer which is polyether-type liquid urethane prepolymer etc,  
 sebacic chloride, telephthalic chloride, isophthalic chloride, azelaic chloride, adipic chloride, etc.

40 According to the present invention, after preparing the primary granules of granule-forming components  
 at the temperature below the cloud point of water-soluble polymer, the obtained suspension liquid is heated  
 to the temperature above the cloud point of the water-soluble polymer and thus oil drops contained in the sus-  
 pension liquid are agglomerated and unified. Therefore when the polymerizable monomer contained in the  
 granule-forming component has the ethylenic unsaturated double bond, it is possible to conduct polymerization  
 45 reaction simultaneously in the agglomeration-unification step by having radical polymerization initiator co-ex-  
 ist. The polymerization initiator to be added may be a generally used oil-soluble peroxide-type or azo-type ini-  
 tiator. For instance, it may be benzoyl peroxide, lauroyl peroxide, 2,2'-azobisisobutyronitrile, 2,2'-azobis-(2,4-  
 dimethylvaleronitrile), etc. The amount of such initiator used is 0.1 ~ 10 wt% preferably 0.5 ~ 5 wt% of the  
 amount of polymerizable monomer.

50 When the polymerizable monomer is a compound which can make interfacial polymerization reaction, it  
 is possible to form polymer layer at the outer shell of the granule by reducing the temperature of suspension  
 liquid to the level below the cloud point of the water soluble polymer in the agglomeration- unification step or  
 after agglomeration-unification step and th n adding the water-soluble compound which can make interfacial  
 polymerization reaction. The water-soluble compound which can make interfacial polymerization r action may  
 55 be 1,6-hexane diamine, 1,4-bis(3-aminopropyl) piperazine, 2-methylpiperazine, m-xylene- $\alpha$ ,  $\alpha'$ -diamine, etc.

The granule forming component of the present invention may contain resin components other than poly-  
 merizable monomer. Such resin components other than polymerizable monomer are not specifically limit d  
 but may be selected out of the resins well-known in the industry according to the characteristics demanded

to the granules obtained. Examples of such resin may be polystyrene resin, polycarbonate resin, polyurethane resin, (meth) acrylic acid ester copolymer, vinyl aromatic compound copolymer such as styrene, polyethylene wax, polypropylene wax, silicone oil and the resin compositions containing said compound.

For the purpose of dissolution of resin component and reduction of viscosity etc, such solvent as xylene, toluene, cyclohexane, ethyl acetate may be co-used with the resin component.

The amount of use of the solvent is preferred to be less than 200 wt parts, more preferably less than 80 wt parts as against 100 wt parts of granule forming component. When the amount of use of the solvent exceeds 200 wt parts, the cost of removal of solvent increases and it is undesirable.

When the granules obtained by the method of the present invention are used for the recording material such as toner, coloring material such as dyestuff or pigment is added to the granule forming component. Such coloring material may be for instance, organic pigment such as copper phthalocyanine, Quinacridone or diazo-yellow or carbon black, magnetic powder etc.

The amount of use of coloring material is preferably 0.5 ~ 150 wt parts as against 100 wt part of granule forming component. When the content of coloring material is less than 0.5 wt parts, its coloring power is inferior and when the content is over 150 wt parts, dispersibility of coloring material decreases.

When the granules obtained are used as toner, it is preferred to use static charge controlling agent such as boron complex, metal complex dye or quaternary ammonium salt together with said coloring material. Amount of use of such static charge controlling agent is preferred to be 0.1 ~ 5 wt parts as against 100 wt parts of granule forming component. When the amount of use is less than 0.1 wt part, static charge controlling effect is insufficient and when it is over 5 wt parts, static charge disperses.

According to the present invention, the suspension liquid is obtained by mixing the aforesaid granule forming component and water solution of polyvinyl alcohol indicating said cloud point and water soluble polymer. The amount of said polyvinyl alcohol and water soluble polymer as against the amount of granule forming component may be properly adjusted for the contents of granule forming component and the objective grain diameter but from the viewpoint of blendability and grain size control, the concentration of the aqueous solution containing polyvinyl alcohol and water soluble polymer is preferred to be 0.02 ~ 15 wt% and the ratio of mixing of granule forming component and water solution of water soluble polymer is preferred to be 1/0.5 ~ 1/3.

When the viscosity of granule forming component and aqueous solution of water soluble polymer is relatively low, an agitator utilizing high speed shearing such as homogenizer may be used for mixing. When the viscosity of granule forming component and water soluble polymer is high, a mixer such as multi-purpose mixer or planetary mixer may be used.

Said polyvinyl alcohol having cloud point at 30 ~ 90°C may be partially saponified polyvinyl alcohol with saponification degree of 60 ~ 85% preferably 70 ~ 80%. It is possible to provide cloud point to polyvinyl alcohol with saponification degree of over 85% which does not by itself indicate cloud point, by addition of electrolytic salt. Since electrolytic salt may be those used as the sedimentation agent of polyvinyl alcohol such as NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub> and such cloud point may be properly adjusted by the amount of addition.

Water soluble polymer having cloud point at 30 ~ 90°C may be cellulose derivative such as methyl cellulose, hydroxypropyl cellulose, polyethylene glycol alkylether or block copolymer of polyethylene glycol-polypropylene glycol and their combinations, which have relatively high solubility in organic solvent when compared to polyvinyl alcohol.

The weight ratio of polyvinyl alcohol and other water soluble polymer in said aqueous solution of water soluble polymer is preferred to be in the range of 99.5/0.5 ~ 10/90. When the ratio of water soluble polymer other than polyvinyl alcohol is less than 0.5, the shapes of the granules obtained do not become uniform and distribution of grain diameter also tends to be wide. When the ratio of water soluble polymer other than polyvinyl alcohol exceeds 90, stability of suspended granules at the temperature above cloud point decreases and large and coarse granules and agglomerating lumps tend to generate.

Said aqueous solution of polyvinyl alcohol and said water solution of water-soluble polymer may be used simultaneously when they are mixed with granule forming component or alternatively, said water-solution of water-soluble polymer may be added after mixing said water solution of polyvinyl alcohol and granule forming component but depending on the molecular weight of polyvinyl alcohol or the kind of said water-soluble polymer, there may exist critical concentration for segregation and they may not dissolve with each other causing difficulty to mixing operation and therefore it is preferred to add the water solution of said water-soluble polymer after mixing said water solution of polyvinyl alcohol and granule forming component.

The cloud point of the aqueous solution of polymer to be set as aforesaid is preferred to be in the range of 30 ~ 90°C particularly in the range of 40 ~ 80°C. When cloud point of water-soluble polymer is less than 30°C, temperature control in the step of adjustment of primary granule becomes difficult. On the other hand, when cloud point is set above 90°C and polymerizable monomer is composed of the double bond of ethylene, polymerization reaction proceeds prior to the agglomeration/unification and viscosity of granule forming com-

ponent increases and agglomerating potency decreases, resulting in the wider distribution of grain diameter. When polymerizable monomer is isocyanate, it causes a vigorous exothermic reaction with water and it is undesirable from safety viewpoint.

In order to increase safety at the temperature above the cloud point of the suspended substance formed as aforesaid, water-soluble polymer which does not indicate cloud point such as hydroxyethyl cellulose or polyvinyl alcohol with saponification degree of over 86% may be added to the suspension liquid. *Solid*

Thus obtained suspension liquid is diluted by ion exchange water to adjust the ultimate content of oily substance to 10 ~ 40 wt%. At the content of less than 10 wt%, economic characteristic is poor and at the content above 40 wt%, distribution of grain diameter widens.

Next the diluted suspension liquid is heated to the agglomeration temperature which is above the cloud point of aqueous solution of polymer, the temperature rising speed being adjusted to 0.4 ~ 2.0°C/min. Such agglomeration temperature depends on the kind of granule forming component and the aqueous solution of polymer. Agglomeration temperature is set in such way that the time required for the oil drops contained in the suspension liquid be formed into the desired grain diameter falls in the range of 5 ~ 75 min.

When it is below 5 minutes, fine particles remain unagglomerated and thus grain diameter distribution widens. When it exceeds 75 minutes, large coarse granules tend to be produced.

Normally when the temperature of the suspension liquid increases, the grain diameter of oil drop increases time-wise. Therefore in order to adjust it to the desired diameter, it is necessary to increase the viscoelasticity of oil drops by completing the reaction of polymerizing monomer and to stop the increase of grain size or when the oil drop is formed to the desired grain size, the suspension liquid is cooled to the temperature below the cloud point of the water soluble polymer and thus stop the growth of oil drops is stopped.

The grain diameter of the enlarged secondary granule is preferred to be 2 ~ 20 times of the diameter of the primary granule. When it is less than twice, grain diameter distribution widens and when it is over 20 times, agglomerated lumps tend to be produced in the system.

By adjusting the grain diameter of the oil drops contained in the suspension liquid utilizing the cloud point of more than two kinds of water soluble polymer, it is possible to obtain the suspension containing the oil drops with remarkably uniform grain diameter when compared to the conventional type suspension. The mechanism of such agglomeration-unification is not clear but it is so estimated that polyvinyl alcohol and other water soluble polymers which exist as the stabilizer of oil drops of granule forming component at the temperature below the cloud point become insoluble in water at the temperature above the cloud point and it causes agglomeration of oil drops in the granule forming component. Then the water soluble polymers other than polyvinyl alcohol existing at the surface of agglomerating oil drops, which have relatively high solubility into granule forming component such as polymerizable monomer work on the unification of oil drops and thus substantially spherical secondary granules are obtained.

To be substantially spherical as aforesaid means that practical Waadel sphericity is in the range of 0.95 ~ 1.00. Here Waadel's practical sphericity is the value represented by the ratio of the diameter of the circle having the area equivalent to the projected area of the granule and the diameter of the minimum circle circumscribing the projected image of the granule.

After the completion of the reaction of polymerizable monomer contained in the granule forming component, the formed resin granules are separated and dried by the well-known method such as filtration or centrifuge. Thus the spherical resin granules with variation coefficient of less than 30% are obtained.

Thus obtained resin granules have such advantageous features, in addition to the said uniformity of shape and grain diameter, that melting temperature control, pigment dispersibility control, grain structure control (microcapsulation, etc.) and surface modification (to provide functional group to the surface of granules) are easy.

When granule forming components contain coloring agents such as carbon black and, upon necessity, polyester resin, vinyl polymer resin and additives such as polypropylene wax, etc., the toner for development of electrostatic image made therefrom has spherical granular shape and narrow grain diameter distribution. Thus obtained toner already has the specified grain diameter distribution and it does not require sorting process employed for toners in general and besides since the granules are spherical, even when they are fine powder of less than 10 µm in diameter, they have such advantageous characteristics as excellent flowability, developing characteristics, transcription characteristics and electrostatic characteristics.

When the substance which can make interfacial polymerization reaction is used as polymerizable monomer, it is possible to form microcapsule-type granules and even when the substance which melts at such low temperature as 90°C ~ 110°C is used for granule forming component, it is possible to obtain the granules having superior storage stability.

Furthermore, by leaving functional groups such as isocyanate group, amino group, carboxylic group, glycidyl group, ethylenic unsaturated bond, etc. remained at the surface of granules and making the granules react therewith, it is possible to modify the surface of the granules with different kind of substances.

### Examples

Hereunder is explained the present invention more concretely on the basis of the Examples but the present invention is not at all limited to these examples.

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#### Example 1

400 g of styrene-n-butyl metacrylate resin (Hymer-SBM-73F manufactured by Sanyo Kasei Kogyo Co.) was dissolved in polymerizable monomer obtained by mixing 420 g of styrene monomer, 175 g of n-butyl acrylate and 5 g of ethylene glycol dimethacrylate followed by addition of 30 g of 2,2'-azobisisobutyronitrile and thus the granule forming component was prepared.

10 Subsequently a polymer solution comprising 35 g of Metolose 65 SH (methyl cellulose manufactured by Shin-Etsu Chemical Co.), 60 g of Gohsenol GH-20 (polyvinyl alcohol with saponification degree of 88% manufactured by Nippon Synthetic Chemical Industry Co.), 15 g Gohsenol KL-05 (poly-vinyl alcohol with saponification degree of 80% manufactured by Nippon Synthetic Chemical Industry Co.) and 1350 g of ion exchange water was added to said granule forming component. Thus obtained mixture was mixed by homoginizer at the rotation frequency of  $10^4$  rpm and thus the suspension containing oil drops with grain size of about  $1.5 \mu$  were prepared.

15 Thus obtained suspension was diluted by addition of 1500 g of ion exchange water and it was transferred to the reaction vessel provided with agitation device, temperature regulator and reflux tube. The suspension was then heated to  $80^\circ\text{C}$  at the speed of  $1^\circ\text{C}/\text{min}$ . and by holding it at this temperature for 6 hrs. the polymerizable monomer was reacted. Thereafter the reaction product was cooled, centrifuged for separation of solid and liquid and dried.

20 When the grain diameter of thus obtained resin granules was measured by Coulter counter, the average grain diameter was  $5.3 \mu\text{m}$ , variation coefficient was 15.0% and the grain size distribution was extremely sharp.

#### Example 2

25 Aqueous solution of polyvinyl alcohol with cloud point of about  $55^\circ\text{C}$  was obtained by adding 50 g of  $\text{Na}_2\text{SO}_4$  to the aqueous solution of polymer comprising 75 g of Gohsenol GH-20 and 900 g of ion exchange water.

30 Thus obtained polyvinyl alcohol solution was added to granule forming component of Example 1 and they were mixed by the same method as in Example 1 and the suspension containing oil drops of about  $1.8 \mu$  in grain diameter was prepared.

35 Then a polymer solution composed of 25 g of hydroxypropyl cellulose (HPC-L manufactured by Nippon Soda Co.) and 2000 g of ion exchange water was added to thus obtained suspension and after such dilution, reaction was conducted in the same manner as in Example 1.

40 Grain diameter of thus obtained resin granules was  $6.8 \mu\text{m}$  variation coefficient was 13.5% and the grain size distribution was extremely sharp.

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#### Example 3

45 A mixture of trimethylol propane, neopentyl glycol, hexahydro-phthalic acid anhydride, isophthalic acid,  $\epsilon$ -caprolacton, with a verage molecular weight of 1300, hydroxyl group value of 210 mg KOH/g, 100 g of Quinacridone Red, 16.0 g of negative charge controlling agent VP-434 (manufactured by Hoechst A.G.) were mixed to prepare the resin component. Thus obtained resin component was added with the mixture of 420 g of tetramethyl xylene diisocyanate (TMXDI manufactured by Takeda Chemical Industries Ltd.) and 80 g of isophorone diisocyanate to obtained the granule forming component.

50 Subsequently, aqueous solution of polymer composed of 75 g of hydroxypropyl cellulose, 60 g of Gohsenol GH-20, 150 g of KL-05 and 1350 g of ion exchange water was added to said granule forming component. Thus obtained mixture was mixed by homoginizer at rotation frequency of  $10^4$  rpm, thus forming the suspension containing oil drops of about  $1.3 \mu\text{m}$  in grain diameter. Thus obtained suspension was diluted by gradually adding 1500 g of ion exchange water and it was transferred to the reaction vessel provided with an agitating device, temperature controller and reflux tube. The reaction vessel was heated to  $65^\circ\text{C}$  at the speed of  $1^\circ\text{C}/\text{min}$ . and after holding it at  $65^\circ\text{C}$  for 15 min. it was water-cooled to  $25^\circ\text{C}$ .

55 Subsequently, 1080 g of 20% aqueous solution of hexamethylene diamine was dropped taking 45 minutes. After dropping is over, it was left standing for 10 min. and 75 g of n-butylamine was further dropped taking another 10 minutes. Thereafter the temperature of the reaction mixtre was set at  $45^\circ\text{C}$  and the xylene used

as solvent was removed by blowing air. Thus obtained residue was centrifuged to separate solid and liquid and after drying, it was crushed to obtain the toner granules. When the grain diameter of thus obtained toner was measured by Coulter counter, the average grain diameter was 6.2  $\mu\text{m}$ , variation coefficient was 18.0% and a toner of Magenta color with extremely sharp grain size distribution was obtained. After mixing 0.6 g of silica granules (AEROSIL R972 manufactured by Nippon Aerosil Co.) as fluidizing agent with 100 g of thus obtained toner, the mixture was further mixed with silicon coated ferrite carrier and the copied image was evaluated by U-Bix 3142 (copying machine manufactured by Konica Co.), a clear image with no fog was obtained.

5 Example 4

10 Copper phthalocyanine is used instead of Quinacridone Red and a mixture of 68 mol% of hexamethylene diamine and 32 mol% of diphenamine D-230 (long chain diamine, molecular weight 230) was used instead of hexamethylene diamine and other than that, the process was conducted in the same way as Example 3 to obtain cyanine colored toner. Grain diameter of thus obtained toner was 5.7  $\mu\text{m}$  and variation coefficient was 15.5%.  
 15 When thermal characteristics of thus obtained toner were measured by using flow tester (manufactured by Shimadzu Seisakusho K.K.), the temperature at which flow-out begins was 106°C. When such toner was left standing for 7 days at 55°C, powder characteristics have undergone no change indicating an excellent storage stability.

20 Example 5

25 A mixed solution of 500 g of polyurethane resin (average molecular weight 1150, 50% xylene solution) comprising hexamethylene diisocyanate, toluene diisocyanate, 2-methyl-1,3-propane diol and 500 g of Takenate D-170HN (manufactured by Takeda Chemical Industries Ltd.) was used as granule forming component and in the same manner as in Example 3, non-soluble gel granules with average grain diameter of 5.5  $\mu\text{m}$ , variation coefficient of 14.5% and not melting up to 300°C were obtained. Such granules are useful as the additive for rheology control.

30 Example 6

35 Aminopyrene is used instead of n-butylamine but otherwise, the process was conducted in the same manner as in, Example 5 and fluorescent granules were obtained. Thus obtained granules were gel granules with the average grain diameter of 5.4  $\mu\text{m}$  and variation coefficient of 14.5%.

40 Example 7

The composition shown below was mixed and it was dispersed by sand grinder mill and thus granule forming component wherein carbon black and polypropylene were favorably dispersed was prepared.

	Components	Amount of mixing (g)
	Styrene-n-butyl methacrylate resin (Hymer SBM-73F)	400
45	Styrene monomer	420
	n-Butyl acrylate	175
	Ethylene glycol dimethacrylate	5
50	Carbon black Printex 150T (manufactured by Degussa AG)	80

5	Electric charge controlling agent Spiro Black TRH (manufactured by Hodogaya Chemical Co.)	10
10	Polypropylene grafted resin obtained in Example 1 of Tokukaihei 1-201676 2,2'-azobisisobutyronitrile	180
15		30

Aqueous solution of polymer was obtained by mixing the following composition with the above.

Components	Amount of mixing (g)
Gohsenol GH-20	75
Gohsenol KL-05	75
Hydroxypropyl cellulose	15
Ion exchange water	1350

25 The mixture of thus obtained granule forming component and aqueous solution of polymer were mixed by planetary mixer to obtain the suspension containing oil drops with average grain size of 2.6 µm. Thus obtained suspension was diluted by 3000 g of ion exchange water and it was transferred to the reaction vessel provided with agitation equipment, temperature controller and reflux tube. Such suspension was heated to 80°C at the speed of 1°C/min and by holding it for 6 hrs. at such temperature, polymerizable monomer was reacted. Thereafter, the reaction product was separated, dried and crushed in the same manner as in Example 1 and black toner granules were obtained.

30 The grain diameter of thus obtained black toner granules was 5.2 µm, variation coefficient was 17.5% and no sorting operation was necessary when it was used as toner. The toner granules are shown in Fig. 1 as an electron micrograph. Grain size distribution of the granules was measured by a Coulter Multisizer and the results are shown in Fig. 2 for weight distribution and Fig. 3 for number distribution.

35 After mixing 3 g of silica granule R-9720 into 100 g such toner, it was mixed with silicon-coated ferrite carrier and image evaluation was conducted by U-Bix 3142 and it was found that a clear image free from off-setting or fog was obtained and fixing was satisfactory.

#### 40 Comparative Example 1

45 Resin granules were obtained in the same manner as in Example 1 except that methyl cellulose was not used. The grain diameter of thus obtained granules was 2.1 µm and although the granules contained those with irregular shape, most of the granules maintained the grain diameter of the primary oil drops in the initial period and grain size distribution was wide.

#### Comparative Example 2

50 Rotation frequency of homogenizer was set at 4000 rpm and the resin granules were obtained in the same manner as Example 3 except that the temperature was not raised. Grain diameter of thus obtained granules was 5.7 µm, variation coefficient was 41% indicating an extremely wide grain size distribution and sorting operation was necessary in order to use them as toner.

#### Comparative Example 3

55 Attempt was made to obtain black toner in the same manner as in Example 7 except that aqueous solution of polymer prepared by mixing the compositions shown in Table 3 was not used but from the time when the temperature was raised to 80°C, agglomerated substances started to stick to the agitation device and reactor

vessel and the granules obtained after completion of reaction were large and coarse agglomerates.

Components	Amount of mixing (g)
Gohsenol KL-05	15
Hydroxypropyl cellulose	150
Ion exchange water	1350

10 There is provided the method which enables to produce spherical resin granules with narrow grain size distribution by adjusting the grain diameter of oil drops contained in the suspension liquid utilizing the cloud points of at least more than 2 kinds of water-soluble polymer.

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**Appendix**

Manufacturing method of (granules) containing polyurea which include,

(a) the step to obtain the emulsion containing oil drops with weight averaged grain diameter of about 0.2 ~ about 0.4  $\mu\text{m}$  by mixing the granule forming components containing 20 ~ 100 wt% of isocyanate compound and aqueous solution containing polyvinyl alcohol having been given cloud point in the range of 30 ~ 90°C by addition of electrolyte to the aqueous solution of polyvinyl alcohol with saponification degree of 60 ~ 85% or polyvinyl alcohol with saponification degree of more than 85%, and aqueous solution containing at least more than one kind of water soluble polymer chosen out of the group composed of methyl cellulose, hydroxy-propyl cellulose, polyethylene glycol alkyl ether and polyethylene glycol-polypropylene glycol block copolymer,

(b) the step to increase the weight averaged grain size of said oil drops by about 2 ~ about 20 times by increasing the temperature of said emulsion to the level above the cloud point of said aqueous solution of polymer,

(c) the step to reduce the temperature of said emulsion to the level below the cloud point and

(d) the step to perform interfacial polymerization by addition of water-solution of amino compound to said emulsion.

**Brief Explanation of the Drawings**

Fig. 1 shows an election microphotograph of the toner granules obtained in Example 7.

Fig. 2 is a graph showing weight grain size distribution of the granules in Example 7.

Fig. 3 is a graph showing number grain size distribution of the granules in Example 7.

**Claims**

1. Manufacturing method of resin granules with grain diameter 1 ~ 100  $\mu\text{m}$  and narrow grain size distribution,

comprising mixing the following three components:

- (a) either polyvinyl alcohol with cloud point at 30 ~ 90°C obtainable by addition of an electrolytic salt to an aqueous solution of polyvinyl alcohol having a saponification degree of more than 85 % or polyvinyl alcohol having a saponification degree of 60 to 85 %, or the both
- 5 (b) an aqueous solution containing at least one kind of water soluble polymer selected from the group consisting of methyl cellulose, hydroxypropyl cellulose, polyethylene glycol alkyl ether and block co-polymer of polyethylene glycol-polypropylene glycol, and
- (c) a granule forming component containing a polymerizing monomer,  
at the temperatures below the cloud point of polyvinyl alcohol and water-soluble polymer, thus obtaining  
10 fine primary granules of less than 10 µm, heating such primary granules to the temperature above said cloud point to obtain by agglomeration and unification of such granules, substantially spherical granules with grain diameter having increased to about 2 ~ 20 times, and then polymerizing them during heating or after formation of granules.
- 15 2. Manufacturing method according to Claim 1 wherein the weight ratio of polyvinyl alcohol having cloud point in the range of 30 ~ 90°C and water soluble polymer having cloud point in the range of 30 ~ 90°C is in the range of 99.5/0.5 ~ 10/90.
- 20 3. Manufacturing method of resin granules with grain diameter 1 to 100 µm and narrow grain size distribution, comprising mixing the following two components:
  - (a) either polyvinyl alcohol with cloud point at 30 to 90°C obtainable by addition of an electrolytic salt to an aqueous solution of polyvinyl alcohol having a saponification degree of more than 85 %, or polyvinyl alcohol having a saponification degree of 60 to 85 %, or the both, and
  - (c) a granule forming component containing a polymerizing monomer  
25 at the temperatures below the cloud point of polyvinyl alcohol and water-soluble polymer mentioned hereinafter, thus obtaining fine primary granules of less than 10 µm, admixing with
  - (b) an aqueous solution containing at least one kind of water soluble polymer selected from the group consisting of methyl cellulose, hydroxypropyl cellulose, polyethylene glycol alkyl ether and block co-polymer of polyethylene glycol-polypropylene glycol,
  - 30 at the temperatures below the cloud point, heating such primary granules to the temperature above said cloud point to obtain, by agglomeration and unification of such granules, substantially spherical granules with grain diameter having increased to about 2 to 20 times, and then polymerizing them during heating or after formation of granules.

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Fig. 1

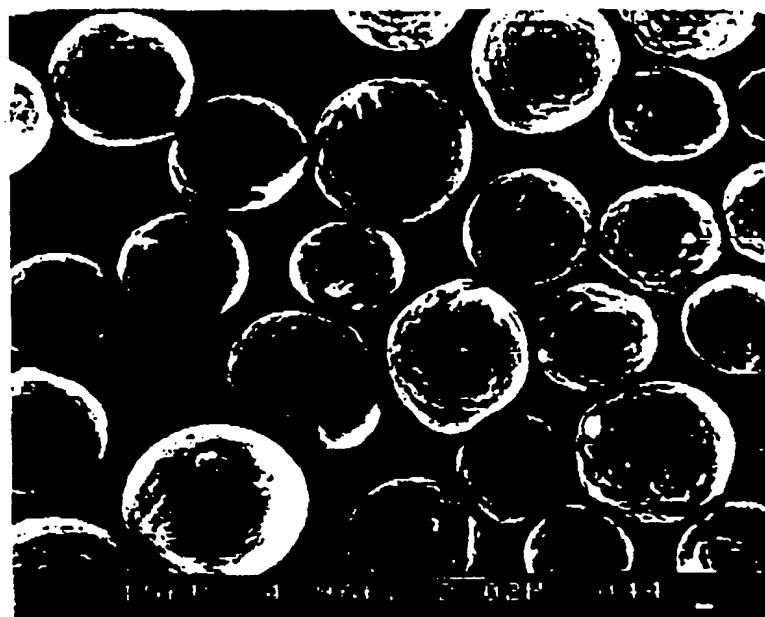


Fig. 2

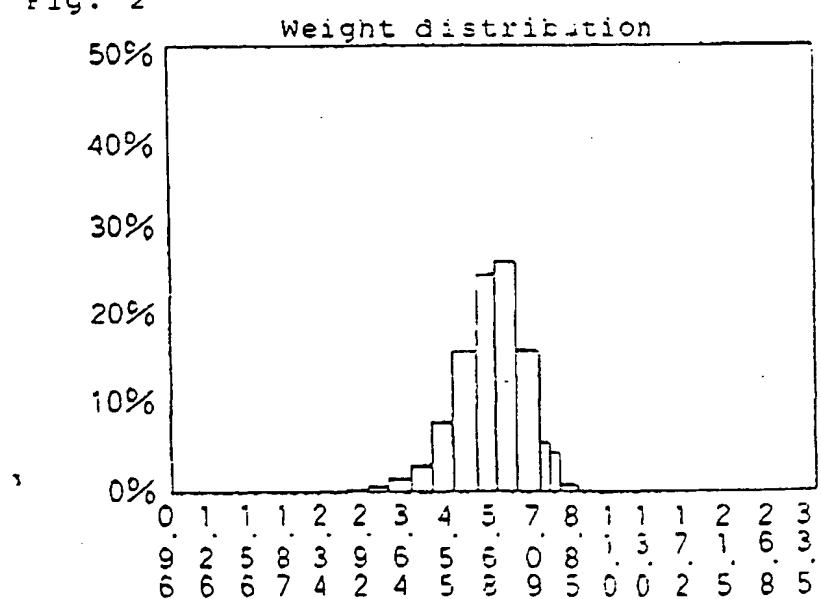
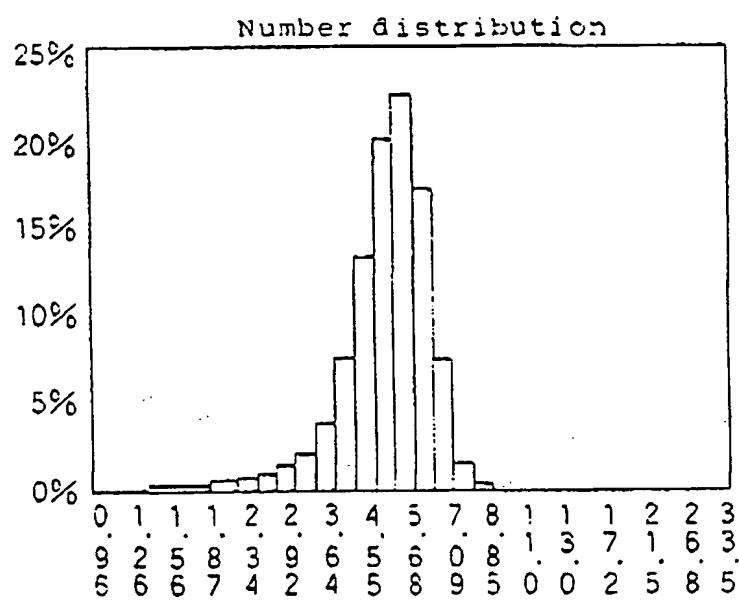


Fig. 3





**European Patent  
Office**

## **EUROPEAN SEARCH REPORT**

**Application Number**

EP 92 11 8503

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 199 859 (FUJIKURA KASEI CO LTD) * claims * * examples * * page 4, line 34 - page 5, line 11 * ---	1-3	G03G9/08 C08F2/20
A	EP-A-0 354 466 (MITSUBISHI RAYON CO. LTD) * claims * * example 1 * ---	1-3	
A	EP-A-0 357 376 (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD) * claims * * examples * * page 6, line 42 - line 55 * -----	1-3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G C08F C08J
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	23 FEBRUARY 1993	PERSSON E.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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